

Metal organic chemical vapor deposition and investigation of ZnO thin films grown on sapphire

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Abstract

A new type of large area metal organic chemical vapor deposition (MOCVD) system for the growth of high quality and large size ZnO materials is introduced. Materials properties of the un-doped, n- and p-doped ZnO epi-films grown on sapphire substrates by this MOCVD system are studied by various techniques, including high resolution X-ray diffraction (XRD), UV–Visible optical transmission (OT), photoluminescence (PL) and photoluminescence excitation (PLE), synchrotron radiation X-ray photoelectron spectroscopy (SR-XPS). The wurtzite (w) ZnO crystal structures grown with primary (0002) orientation were identified. Results have shown the high crystalline quality of MOCVD-grown ZnO films, indicated by the narrow XRD, PL and Raman line widths, strong PL signals, sharp OT edge and smooth surface. In particular, high p-type carrier concentration of $>10^{17} \text{ cm}^{-3}$ have been achieved besides the good n-type doping in ZnO.

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1. Introduction

Recently, there arises much interest in the research and development on ZnO and related materials. ZnO possesses a room temperature (RT) wide directly band gap of about 3.37 eV [1] and a large exciton binding energy of 59 meV ($>$ GaN of 28 meV) that make it suitable to applications in light emitting diodes (LEDs), lasers, solar cell, and transparent transistors [1–15]. These applications require high quality ZnO materials with good uniformity and controllable for thickness and doping level (in both n and p-type). Metal organic chemical vapor deposition (MOCVD) is an excellent technology to achieve above applications and requirements.

The advantage should translate to an even brighter light emission than that obtained with GaN photonics. Un-doped ZnO typically exhibits n-type conductivity, and can be made strongly n-type by growth in zinc-rich conditions or by extrinsic doping

with group-III elements such as Al, Ga or In [16]. For ZnO thin films, n-type conductivity is relatively easy to realize. Until recently, ZnO thin films have proven difficult to dope p-type. This is a fairly common occurrence in wide band-gap semiconductors. In ZnO thin films, most candidate p-type dopants introduce deep acceptor levels. For example, Cu introduces an acceptor level with energy 0.17 eV below the conduction band.

New ZnO-MOCVD systems and process technologies for single and multi-component oxides have been developed recently at Structured Materials Industries, Inc. (SMI) [17]. This paper reports on the MOCVD growth and characterization of a series of ZnO epi-films, un-doped, n-type, and p-type, grown on sapphire by using a new 6 by 2 inch wafer ZnO-MOCVD system under different growth conditions. This reactor uses new patent pending multi-zone filament heater technology — including a shaft heater. In parallel work, this reactor design has also been scaled to deposit on 38–2 inch wafers per deposition run. A variety of techniques, including the high resolution X-ray diffraction (XRD), synchrotron radiation X-ray photoelectron spectroscopy (SR-XPS), optical transmission (OT), photoluminescence (PL), and photoluminescence excitation (PLE) have been employed to investigate their

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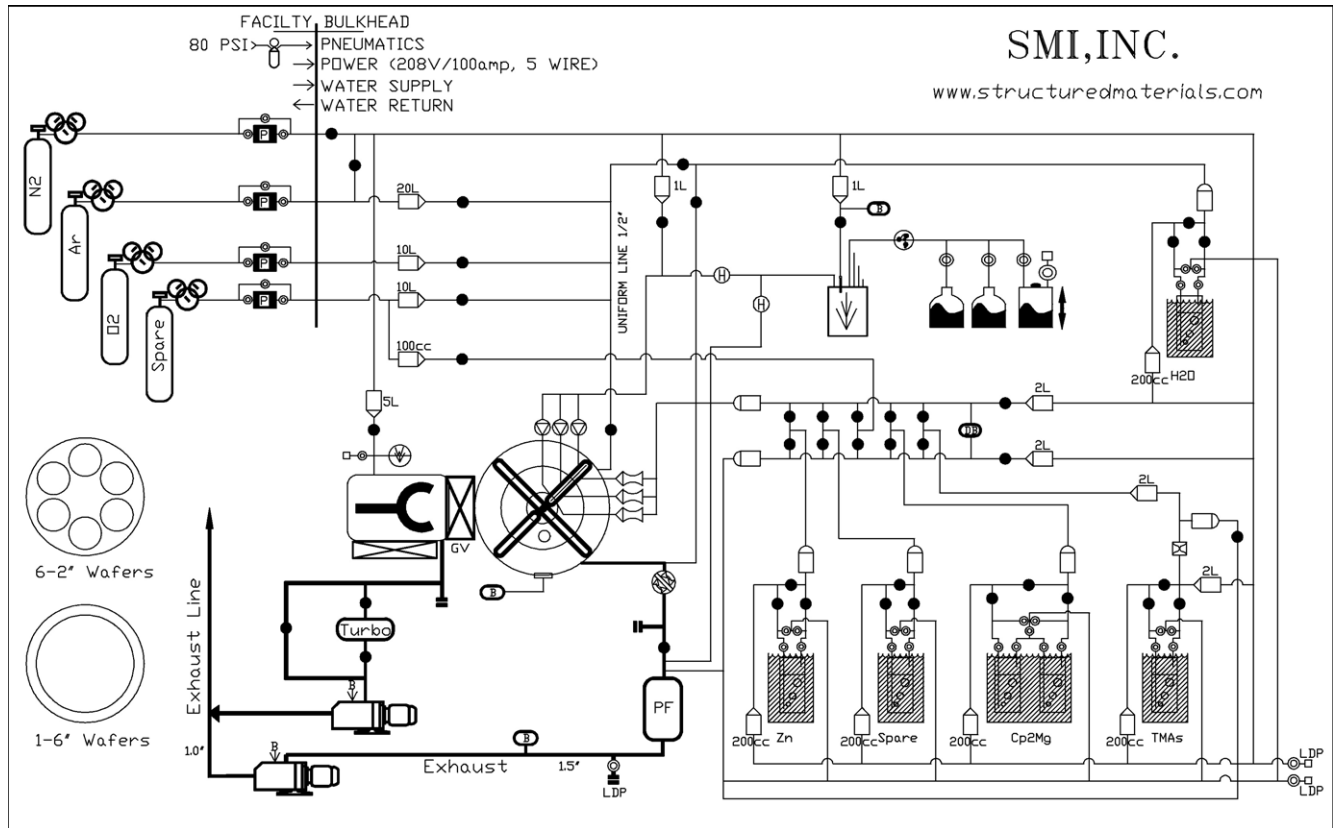


Fig. 1. Schematics of a ZnO MOCVD system designed by Structured Materials Industries, Inc (SMI).

optical and structural properties. These experiment results provide useful information about fabrication of ZnO thin film materials.

2. Experiment

A zinc oxide MOCVD system is designed and built by Structured Materials Industries (SMI). Fig. 1 shows its schematic diagram. The reactor uses the vertical growth configuration with a high speed rotation disk. It is of a vertical orientation built to all metal UHV standards. Metalorganics are used for zinc and dopant sources which are to optimize performance at low pressures. The tools can produce amorphous/poly or epitaxy uniform ZnO with controllable doping and smooth, pinhole-free films, or nanowires, based on process conditions. The precursors used for the MOCVD growth of ZnO and related conditions are offered by SMI as shown in Table 1. General process condition ranges, using such precursors, are as follows: growth pressure from a few Torr to a few tens of Torr, total flows from a few thousand sccm to several thousand sccm, film deposition temperature from 350 °C to 650 °C for general contact work, and precursor rate limiting species pressure (in the reactor) from about 10 mTorr to 50 mTorr.

In order to enhance N incorporation into the depositing film, SMI has used plasma activation. SMI accomplished this using an upstream plasma source, enhancing the availability and reactivity of nitrogen radicals to the depositing film, thus increasing the incorporation/activation rate. This deposition approach is superior

to the prior art because SMI's system is designed to exert independent process control over each of the process parameters, which include physical distribution of the reactants within the reactor, level of activation of the reactants (i.e. degree of nitrogen and/or oxygen plasma activation independent of carrier, other

Table 1
Precursors used for the MOCVD growth of ZnO

Precursor	Vp/t	Comments
<i>Precursor</i>		
Diethyl zinc	15.9 T/25 °C	
<i>Alloying elements: Mg, Cd, Mn</i>		
Cp ₂ Mg	0.35 T/50 °C	Temp. sensitive
Dimethyl cadmium	108.2 T/25 °C	
Cp ₂ Mn, Mn (thd) ₃	Low vp	Cp ₂ Mn: toxic; thd, use FE
<i>n-type dopants: Al, Ga, F</i>		
Trimethyl aluminum	11.5 T/25 °C	
Trimethyl gallium	226.5 T/25 °C	
Triethyl gallium	6.73 T/25 °C	Easier for doping than TMGa
HF	Gas	Corrosive
<i>p-type dopants: P, As, N, Li</i>		
Tert-butyl phosphine	263.98 T/25 °C	
Tert-butyl arsine	151.09 T/25 °C	
Triethyl arsine	8.21 T/25 °C	Easier for doping than TBA
Li tert-butoxide	0.01 T/110 °C	Semi-insulating dopant
N ₂ , N ₂ O, NH ₃ , NO	Gases	Plasma usu. necessary

oxidizer and metalorganics), partial pressures of each process gas, deposition pressure, deposition temperature, and so on. We used the X-ray diffraction (XRD), synchrotron radiation X-ray photoelectron spectroscopy (SR-XPS), optical transmission (OT), photoluminescence (PL), and photoluminescence excitation (PLE) to characterize the material properties and compare the difference of the obtained spectra to define the quality of the samples.

3. Results and discussion

3.1. Optical transmission (OT)

Fig. 2 shows the UV–visible optical transmission spectra of ZnO, undoped, p-type and n-type, measured at room temperature (RT). Fig. 3 shows the determination of the optical gap, E_{og} , from UV–Visible transmission, for these three ZnO films grown on sapphire by MOCVD.

3.2. Photoluminescence (PL)

Fig. 4 shows the PL spectra, excited under a HeCd 325 nm laser line, for four ZnO films grown on sapphire by MOCVD. Three samples, undoped, p-doped and one n-doped, possess a PL peak at ~ 3.28 eV, characteristic of the band edge emission from wurtzite ZnO crystal. Another n-type ZnO sample #126, with the spectrum at the bottom curve in Fig. 4, shows the PL peak shift from 3.28 eV to 3.38 eV in comparison with the ZnO #127, which indicates a high doping level of this ZnO film. This PL peak shift can be also induced by different amount of strains within the ZnO film [18,19]. PL spectra show change with annealing.

3.3. Photoluminescence excitation (PLE)

Figs. 5 and 6 show the photoluminescence excitation (PLE), plus PL for comparison, spectra from two MOCVD-grown ZnO films grown on bulk ZnO and sapphire, respectively. These PLE and combined PL measurements were performed via a J-Y commercial system using a white light Xe lamp source. Different PL excitation wavelengths and different PLE detection wavelengths were used to exhibit more significant

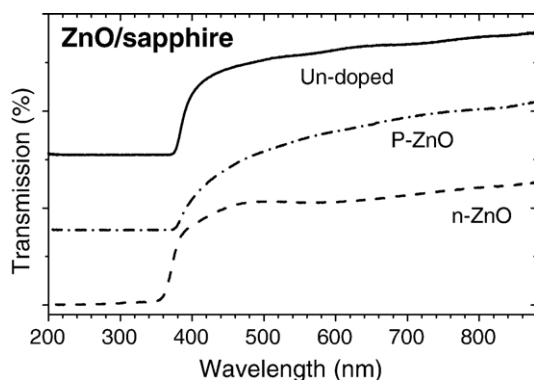


Fig. 2. UV–Visible transmission of three ZnO films grown on sapphire by MOCVD.

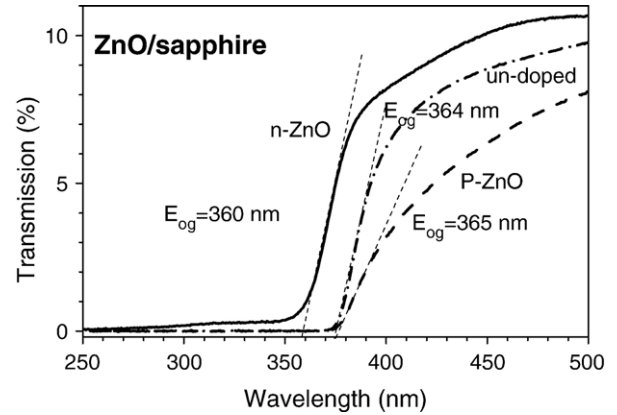


Fig. 3. Determination of the optical gap, E_{og} , from UV–Visible transmission, for three ZnO films grown on sapphire by MOCVD.

spectral features for two experimental samples. For the MOCVD-grown ZnO film on ZnO substrate, PL spectrum in Fig. 5 (a) with the excitation of 320 nm, above the band gap of ZnO, exhibits the near band edge emission with the peak at 376 nm and broad features in the green spectral range. As using the excitation of 380 nm, i.e. near the ZnO band gap, the broad green emissions with the peak at ~ 511 nm are shown. While the PLE spectra for this ZnO/ZnO sample shows the high excited state broad absorption near 279 nm, i.e. 4.4 eV at detection of 376 nm (Fig. 5 (c)), i.e. the peak energy of the band edge PL emission, and an absorption band at 386 nm, i.e. slightly below the ZnO band gap, at detection of 500 nm, i.e. on the top of the green emission band (Fig. 6 (d)).

For the MOCVD-grown p-type ZnO film on sapphire substrate, PL spectrum in Fig. 6 (a) under the excitation of 280 nm, above the band gap of ZnO, exhibits the ZnO band edge emission at 376 nm and two features at 416 nm and 438 nm. As using the excitation of 376 nm at the ZnO band gap or the top of band edge emission, these two spectral features are still seen, plus broad emissions covering green-origin-red (Fig. 6 (d)).

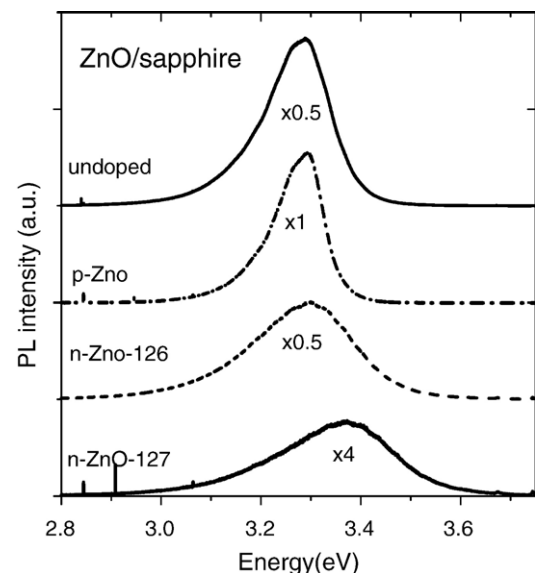


Fig. 4. Micro-PL spectra, excited under 325 nm, of the undoped, p-type and n-type ZnO films grown on sapphire substrates by MOCVD.

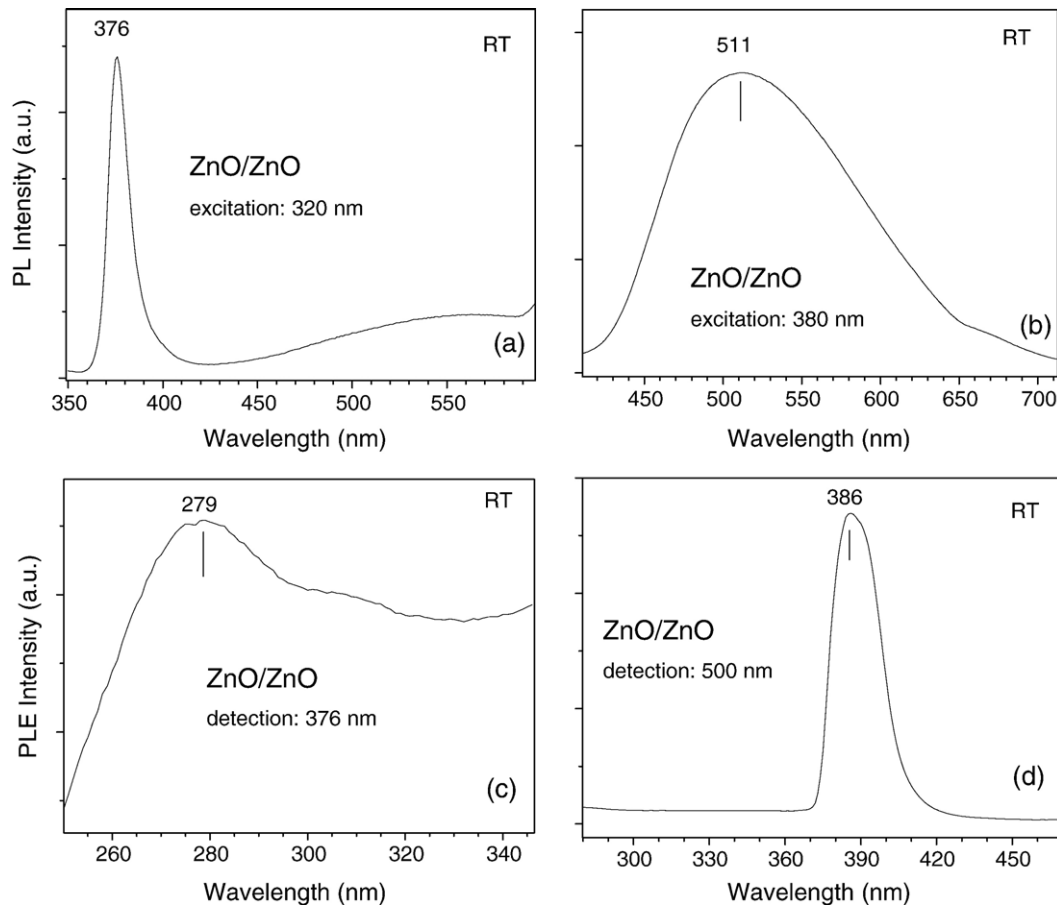


Fig. 5. PL and PLE of ZnO film grown on bulk ZnO substrate.

While the PLE spectra for this ZnO/sapphire sample shows the high excited state broad absorption near 279 nm, i.e. 4.4 eV at detection of 376 nm (Fig. 6 (c)), i.e. the peak energy of the band edge PL emission, and an absorption band at 386 nm, i.e. slightly below the ZnO band gap, at detection of 500 nm, i.e. on the top of the green emission band (Fig. 6 (d)).

3.4. Visible Raman scattering

Fig. 7 shows the micro-Raman scattering spectra for three ZnO films, under the excitation of 488 nm from an Ar⁺ laser. A sharp peak at 437 cm⁻¹ is observed for all ZnO samples, which is the wurtzite ZnO characteristic E₂ mode. The intensity and full width at half maximum (FWHM) of the E₂ mode was employed to represent the quality of ZnO materials. Higher intensity, narrow and symmetric features indicate the quality of our MOCVD-grown ZnO films on sapphire substrate with high crystalline quality.

3.5. Resonant Raman scattering

Raman scattering measurements on our experimental ZnO samples were also performed using UV excitation of 325 nm from a HeCd laser. Fig. 8 shows These Raman spectra for three ZnO films. As seen, a strong A₁ symmetry longitudinal optical (LO) phonon mode, 1LO at 556 cm⁻¹, and its second order 2LO

mode are observed for all samples. The spectral rising in the high frequency side in Fig. 8 is from the ZnO edge mission PL band. In comparison with the visible Raman spectra of Fig. 7 under the 488 nm excitation, where no A₁(LO) and 2LO modes could be detected. Now, under the UV 325 nm excitation beyond the ZnO band gap, the PL band tail has induced and enhanced the A₁(LO) and 2LO modes through the resonant Raman scattering process.

3.6. Synchrotron radiation X-ray photoelectron spectroscopy (SR-XPS)

In order to study the surface oxidizations and estimate the degree of pollutions by carbon, we arrange a synchrotron radiation X-ray photoelectron spectroscopy (SR-XPS) experiments on the 24A1 beamline of National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan (R.O.C.). SR-XPS experiments were performed using a monochromatic X-rays beam with 1150 eV incident light energy. The constant analyzer energy (CAE) mode was used with analyzer pass energy of 200 eV for preliminary wide scan (Fig. 9). The binding energy of C 1s, O 1s, and Zn 2p were observed at 285.01, 531.01, and 1020 eV, respectively.

4. Conclusion

In this paper, a new type of metalorganic chemical vapor deposition (MOCVD) system for the growth of high quality and

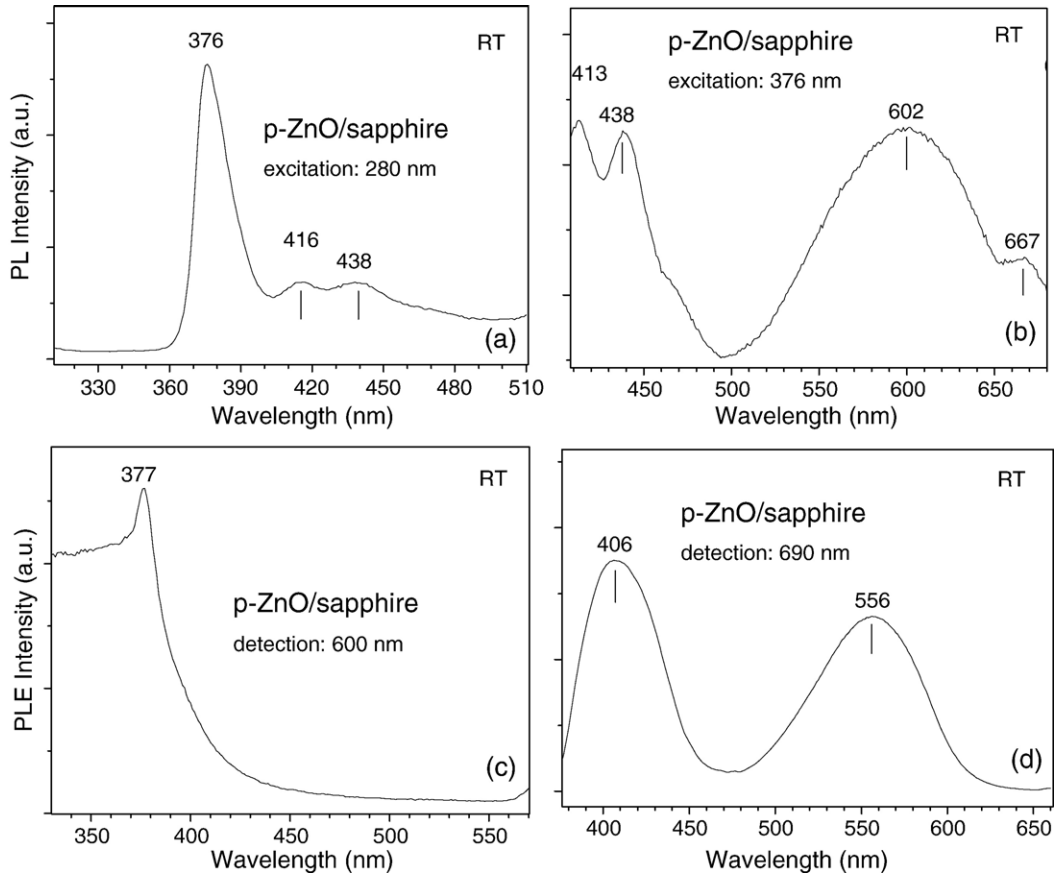


Fig. 6. PL and PLE of p-type ZnO film grown on sapphire substrate.

large size ZnO materials is introduced. Materials properties of the un-doped, n- and p-doped ZnO epi-films grown on sapphire substrates by this MOCVD system are reported. Materials were characterized by various techniques. Photoluminescence (PL) indicated the w-ZnO band edge emission band near 3.3 eV and the variation of the PL peak with the doping levels. UV–Visible optical transmission (OT) measurements gave the optical gap values, corresponding to the PL results. Visible Raman scattering showed the w-ZnO characteristic E_2 phonon mode and UV 325 nm excited resonant Raman scattering exhibited the $A_1(\text{LO})$ and 2LO phonon modes which were enhanced due to the resonance with the fundamental ZnO PL band.

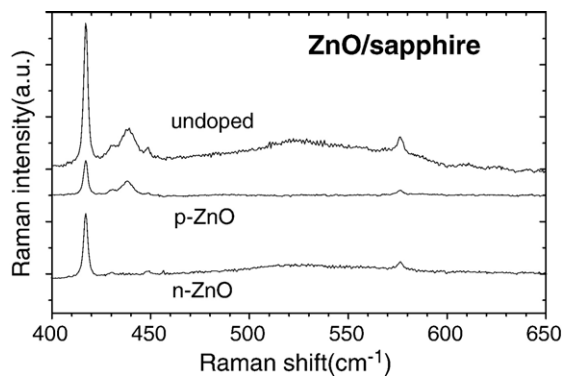


Fig. 7. Raman spectra of three MOCVD-grown ZnO under the excitation of 488 nm.

Synchrotron radiation X-ray photoelectron spectroscopy (SR-XPS) showed the surface oxidizations and estimated the degree of pollutions by carbon.

All results have shown the high crystalline quality of MOCVD-grown ZnO films, indicated by the narrow XRD, PL and Raman line widths, strong PL signals, sharp OT edge and smooth surface. In particular, high p-type carrier concentration of up to 10^{19} cm^{-3} has been achieved besides the good n-type doping in ZnO. New classes of p–n junction devices based on ZnO including blue and UV LEDs, lasers and detectors are

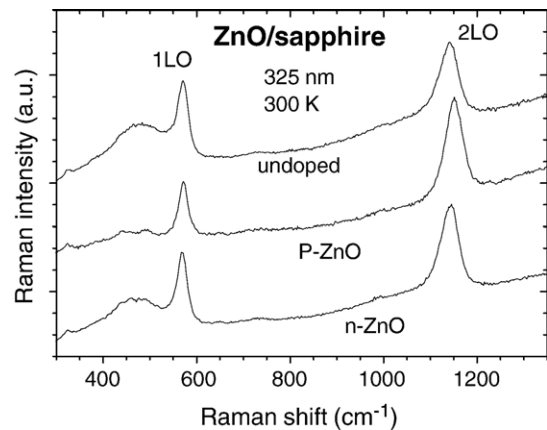


Fig. 8. Resonant Raman spectra of three MOCVD-grown ZnO under the excitation of 325 nm.

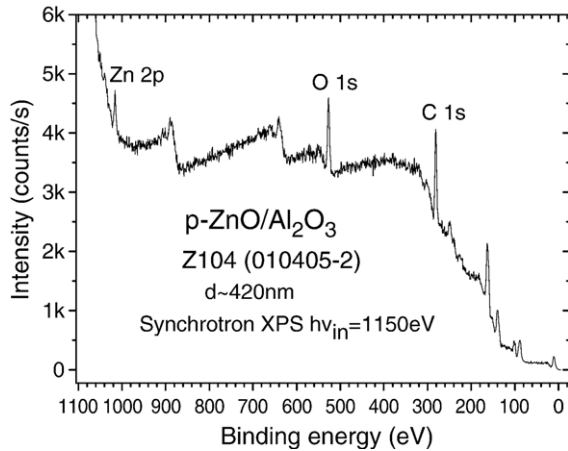


Fig. 9. Synchrotron radiation XPS of the p-type ZnO film grown on sapphire substrate.

expected, based upon our excellent ZnO MOCVD systems and optimization of growth conditions.

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